

## CLAIMS

*What is claimed is*

1. A method of depositing a solid material on a substrate having gaps of dimension on the order of about 100 nanometers or less, the method comprising:
  - (a) exposing the substrate to a precursor of the solid material, which is in the vapor phase in order to achieve selective condensation in narrow gaps where the precursor is liquefied due to the Kelvin effect.
  - (b) converting the liquid regions of precursor to the solid material in the gaps.
2. The method of claim 1, wherein the solid material is a dielectric material.
3. The method of claim 2, wherein the dielectric material is a silicon oxide.
4. The method of claim 1, wherein the solid material is a metal.
5. The method of claim 1, wherein the substrate is a partially fabricated semiconductor device.
6. The method of claim 5, wherein the solid material comprises an interlayer dielectric formed between active devices and a first metallization layer, and wherein the gaps are regions between gates of adjacent active devices.
7. The method of claim 5, wherein the solid material comprises dielectric for shallow trench isolation and the gaps are trenches around active devices.
8. The method of claim 5, wherein the solid material is a metal for conductive lines and the gaps are trenches and/or vias defining paths for the conductive lines in a dielectric layer.

9. The method of claim 1, wherein the precursor is a precursor of a dielectric material.
10. The method of 9 wherein the dielectric material is a silicon containing dielectric material.
11. The method of claim 9, wherein the precursor of the dielectric material comprises one of more compounds selected from the list comprising tetraethylorthosilane (TEOS), tetramethoxysilane (TMOS), methyl triethoxysilane (MTEOS), methyltrimethoxysilane (MTMOS), dimethyldimethoxysilane (DMDMOS), trimethylmethoxysilane (TMMOS), dimethyldiethoxysilane (DMDEOS), bis-triethoxysilyl ethane (BTEOSE) or bis-triethoxysilyl methane (BTEOSM), tetramethylcyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), and tetravinyltetramethylcyclotetrasiloxane (TVTMCTS).
12. The method of claim 1, wherein the precursor is a precursor of a metal.
13. The method of claim 12, wherein the precursor of a metal comprises a copper containing precursor selected from the list comprising copper (II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ ), copper (II) hexafluoro-acetylacetonate ( $\text{Cu}(\text{hfac})_2$ ), copper (I) hexafluoro-acetylacetonate trimethylvinylsilane ( $\text{Cu}(\text{hfac})(\text{TMVS})$ ), hexafluoro-pentadionato(vinyltrimethoxysilane)copper (I) ( $(\text{hfac})\text{Cu}(\text{VTMOS})$ ), hexafluoro-pentadionato(cyclooctadiene) copper (I) ( $(\text{hfac})\text{Cu}(\text{COD})$ ), hexafluoro-pentadionato(dimethylethylamine)copper (I) ( $(\text{hfac})\text{Cu}(\text{DMEA})$ ), hexafluoro-pentadionato(1-pentene)copper (I) ( $(\text{hfac})\text{Cu}(\text{1-pentene})$ ), copper (II) tetramethyl heptanedionate ( $\text{Cu}(\text{TMHD})_2$ ), and copper trimethyl octanedionate ( $\text{Cu}(\text{TMOD})_2$ ).
14. The method of claim 12, wherein the precursor of the metal is an aluminum-containing precursor selected from the group consisting of aluminum alkyls, aluminum alkyl hydrides, and alane complexes.
15. The method of claim 14, wherein the aluminum alkyl is selected from the group consisting of triisobutylaluminum (TIBA), and trimethylaluminum (TMA)

16. The method of claim 14, wherein the aluminum alkyl hydride is dimethylaluminum hydride (DMAH)

17. The method of claim 14 wherein the alane complex is selected from the group comprising dimethylethylamine alane (DMEAA), methylpyrrolidine alane (MPA), and trimethylamine alane (TMAA)

18. The method of claim 11, wherein the precursor of a metal comprises a tungsten metal halide.

19. The method of claim 18, wherein the tungsten metal halide is tungsten hexafluoride (WF<sub>6</sub>).

20. The method of claim 1, wherein (a) comprises contacting the substrate with the precursor in vapor phase to a partial pressure at or below the saturation pressure of the precursor to thereby form liquid regions in the gaps without substantial condensation in the field.

21. The method of claim 1, wherein (a) comprises contacting the substrate with the precursor in vapor phase at a partial pressure of at least about the saturation pressure of the precursor to thereby form the liquid regions in at least the gaps.

22. The method of claim 21, wherein (a) further comprises subsequently reducing the partial pressure of the precursor to a level below its saturation pressure and above a hysteresis pressure at which a minimal amount of the precursor remains in liquid phase in the gaps.

23. A method of claim 1, wherein (a) comprises contacting the substrate with the precursor in liquid form in a process from the group including spin casting, spray on, print on, and dip casting.

24. The method of claim 23, wherein (a) further comprises subsequently reducing the partial pressure of the precursor to a level below its saturation pressure and above

a hysteresis pressure at which the bulk liquid evaporates but a minimal amount of the precursor remains in liquid phase in the gaps.

25. The method of claim 1, wherein the converting in (b) comprises reacting the precursor liquid regions with another material to produce the solid material.

26. The method of claim 1, wherein the converting in (b) comprises decomposing the precursor in the liquid regions to produce the solid material.

27. The method of claim 1, wherein the converting in (b) comprises solidification by cooling to a temperature below the melting point of the precursor.

28. The method of claim 1, wherein the gaps have reentrant features.

29. The method of claim 1, wherein the gaps have vertical sidewalls.

30. The method of claim 1, wherein (a) and (b) are repeated in order to fill gaps not previously filled in one cycle.

31. The method of claim 1, further comprising depositing additional solid material on the substrate in features that were not previously filled, wherein the substrate comprises gaps having dimensions significantly greater than about 100 nanometers.

32. The method of claim 31, wherein depositing the additional material comprises a process selected from the group comprising of chemical vapor deposition (CVD), atomic layer deposition (ALD), high density plasma (HDP), plasma assisted chemical vapor deposition (PECVD), subatmospheric chemical vapor deposition (SACVD), pulsed nucleation layer (PNL) deposition, pulsed deposition layer (PDL) deposition, electroplating, electroless plating, and spin-on, spray-on, and print-on methods.

33. A method of depositing a solid material on a substrate having gaps of dimension on the order of about 100 nanometers or less, the method comprising:

(a) exposing the substrate a vapor phase precursor of the solid material, wherein the precursor has a first partial pressure of at least about its saturation pressure in the environment of the substrate;

(b) maintaining the partial pressure of the vapor phase precursor at the first partial pressure until at the precursor condenses to form liquid regions in the gaps and in regions outside the gaps;

(c) reducing the partial pressure of the vapor phase precursor to a second partial pressure below its saturation pressure but above a hysteresis pressure;

(d) maintaining the partial pressure of the vapor phase precursor at the second partial pressure such that the liquid precursor in the regions outside the gaps vaporizes, while at least a minimal amount of the liquid phase precursor remains in the gaps; and

(e) converting the liquid regions of precursor remaining in the gaps to the solid material in the gaps.

34. The method of claim 33, wherein the partial pressure of the vapor phase precursor is adjusted by adjusting the flow rate of a diluent gas.

35. The method of claim 33, wherein the partial pressure of the vapor phase precursor is adjusted by adjusting the flow rate of the vapor phase precursor.

36. The method of claim 35, wherein adjusting the flow rate of the vapor phase precursor comprises adjusting the temperature of a source of the precursor.

37. A method of depositing a solid material on a substrate having gaps of dimension on the order of about 100 nanometers or less, the method comprising:

(a) exposing the substrate to a vapor phase precursor of the solid material under conditions in which the precursor selectively forms liquid regions in at least some of the gaps, wherein the vapor phase precursor has a partial pressure below its saturation pressure; and

(b) converting the liquid regions of precursor to the solid material in the gaps.

38. The method of claim 37, wherein (a) comprises:

(i) condensing the precursor on the substrate, whereby the precursor forms liquid regions in at least some of the gaps and in regions outside the gaps;

(ii) evaporating the liquid precursor from regions outside the gaps while maintaining at least some of the liquid regions in the gaps by lowering the partial pressure of the vapor phase precursor to a point below its saturation pressure.

39. The method of claim 37, wherein (a) comprises condensing the precursor on the substrate to selectively form liquid regions in at least some of the gaps, but not outside the gaps, by providing the vapor phase precursor at a partial pressure approaching its saturation pressure.